Indian J. Phys. **68A** (6), 521 – 528 (1994)

I J P A
— an international journal

Characterization of chalcohalide $(As_2Se_3)_{95}I_5$ semiconductor glass

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Received 15 March 1994, accepted 3 September 1994

Abstract : Chalcohalide glasses are relatively uncommon inorganic glasses compared to chalcogenide and halide glasses In the present work, As_2Se_3 and $(As_2Se_3)_{95}I_5$ glasses have been prepared and analyzed by different techniques (X-ray powder diffraction density determination, vicker hardness and thermal analysis) Also the temperature dependence of the dc conductivity as well as the optical absorption at room temperature have been measured

Keywords : Amorphous semiconductors, chalcogenide and chalcohalide glasses, preparation and analysis

PACS Nos. : 61 10 Lx, 72 20 –i, 78 66 Jg

1. Introduction

Chalcogenide and halide glasses have attracted a great deal of attention during the past 30 years because of their special IR properties.

Chalcogenide (sulfide, selenide and telluride) glasses are well known for their chemical durability and mid IR transmittance up to 15 μm. However, these glasses possess high refractive indices and intrinsic optical loss, as well as contamination from parasitic absorption by groups such as OH, SH, *etc*. On the other hand, the relatively poor chemical durability of halide glasses [1] together with their low-glass transition temperatures, pose serious problems for practical application. The structural aspect is interesting from a fundamental view point since chalcogenide glasses are predominantly covalent and halide glasses are predominantly ionic in character.

At first sight, it might seem possible to improve the chemical durability of halide glasses by incorporation into a chalcogenide glass. Secondly, a possible decrease in the refractive index of the chalcogenide glass would reduce the intrinsic scattering losses in the IR [2].

Since halide and chalcogenide glasses are both transparent in the IR region, it is probable that the mixed chalcohalide glasses are IR transmitting also. Pioneering work on chalcohalide glasses were carried out in 1960 by Flascher *et al* [3], Pearson [4], Hopkins *et al* [5] and Dembovskii *et al* [6], mainly concerned on ternary glassy systems, such as As–S–X, Ge–S–X, Sb–S–X (X is Cl, Br or I). Also, the glass formation and optical properties of multi-component chalcohalide glasses based on AsSe–AsTe–PbCl–Tl were studied in 1960 [7]. A general review of the properties of chalcohalide has been provided by different authors [1,8,9] in the literature.

In chalcohalide systems, the anions have a great influence on chemical bond characteristics and also on glass formation. It seems that closer the electronegativity value between group VI and group VII elements, the more easy is the formation of chalcohalide glasses.

2. Experimental techniques

2.1 Material preparation :

2.1.1. Bulk material

Firstly, As_2Se_3 was prepared from highly pure arsenic and selenium (99.999%) by placing the appropriate proportions into fused silica tubes sealed under 10^{-5} torr. The evacuated tube was then placed in a furnace and the temperature was raised in steps to 800°C. The synthesis time was about 4 hrs, during which the molten material was vigorously shaked. At the end of the synthesis process, the molten material was quenched in ice-water mixture. The ternary $(As_2Se_3)_{95}I_5$ was prepared from the binary As_2Se_3 by adding the correct amount of iodine and maintaining at 600°C for 6 hrs in an evacuated (10^{-5} torr) silica tube. The ampoule was occasionally shaken during the synthesising period to ensure homogeneity of the material Quenching was then carried out in air for few seconds followed by immersion in ice-water mixture (to ensure less porosity within the obtained samples).

2.1.2. Thin film

The electron beam evaporation was chosen for preparing the thin film sample. An Edward 306A coating unit with a carbon boat was used for evaporation. The thickness of the sample was 5000 Å.

2.2. Measurement techniques :

The amorphous character of the investigated samples was confirmed by Philips X-ray diffractometer (PW 1140190) with X-ray goniometer of the type PW 1373. Thermal experiments were carried out on a Shimadzu instrument (type DT-50). The differential scanning calorimetry (DSC) measurements were carried out in a nitrogen atmosphere (50 ml/min), using α-Al_2O_3 as the reference material. Thermogravemetric (TGA) measurements were also performed to evaluate the activation energy of decomposition using the method proposed by Ozawa [9]. In this method, TGA curves were obtained at different heating rates (Φ's) and the following equation was used to obtain E_d

$$\log \Phi_1 + 0.4568E_d/RT_1 = \log \Phi_2 + 0.4567E_d/RT_2 = \quad ,$$

where T(K) is the temperature at which the sample is decomposed at a heating rate Φ. In the above equation, when the common logarithms of the heating rates are plotted against the reciprocal of absolute temperatures, a straight line will be obtained in the range where the decomposed ratios are equal. Accordingly, the activation energy of decomposition E_d can be evaluated from the slope of the line.

Measurements of dc conductivity were made in a dry nitrogen atmosphere using specially designed cells provided with a temperature-controlling system in the temperature range from 160 K to below T_g of the sample. Keithly 616 digital electrometer was used for measurements of correct down to 10^{-14} amp.

The vickers microhardness of the glasses (V_H) was measured at room temperature, using a vickers microhardness tester (Shimadzu type-M) attached to a data processor (Shimadzu Dutaletty 150)

The optical absorption was measured at room temperature using Uvikon 860 Kontron.

3. Results and discussion

3.1. Physical properties :

The XRD patterns of the prepared powder glasses As_2Se_3 and $(As_2Se_3)_{95}I_5$ are shown in Figure 1. The figure shows that the samples are amorphous.

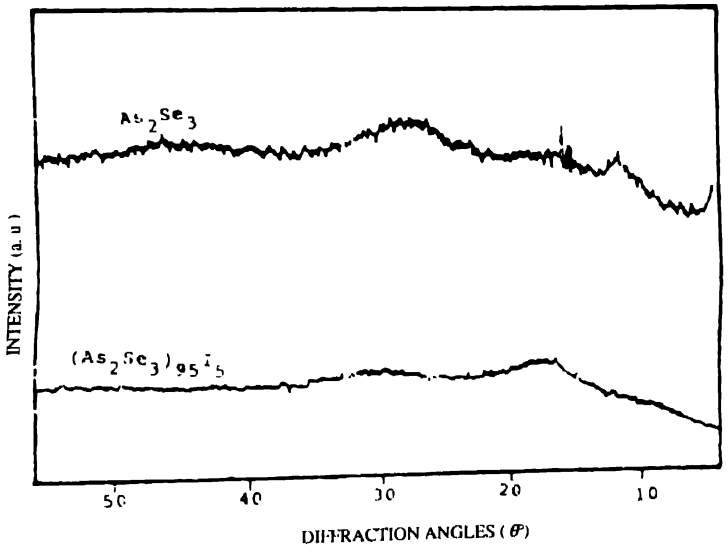

Figure 1. X-ray diffraction patterns for the glasses As_2Se_3 and $(As_2Se_3)_{95}I_5$

Figure 2 shows DSC thermograms for the two glasses measured at a constant heating rate of 20 deg/min. The figure shows the three phenomena of interest : the glass transition (at

a temperature T_g), the crystallization exotherm (with the maximum crystallization at the temperature T_c) and the melting endotherm (with a melting point T_m). The glass transition

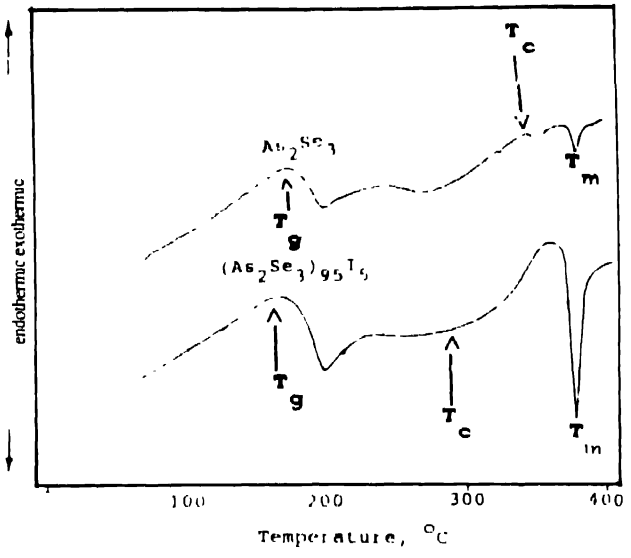

Figure 2. DTA thermograms of As_2Se_3 and $(As_2Se_3)_{95}I_5$ glasses

occurred at 177°C for As_2Se_3 and at 154°C for $(As_2Se_3)_{95}I_5$. After T_g, the exothermic peak, due to crystallization starts at temperature 333°C for As_2Se_3 and at 297°C for $(As_2Se_3)_{95}I_5$. The endothermic peak due to melting occurred at 375°C for As_2Se_3 and 371.5°C for $(As_2Se_3)_{95}I_5$.

The density (d) of the as-prepared glassy As_2Se_3 and $(As_2Se_3)_{95}I_5$ samples was determined by the hydrostatic method and the results are 4.49 and 4.47 gm/cm^3 respectively. The measurements for each composition were carried out on three different parts of the same ingot. The d values obtained were reproducible within 0.05%, indicating high homogeneity of the quenched ingots.

The value of vickers hardness (V_H) decreases from 137.7 (As_2Se_3) to 136 Kgm mm^{-2} ($(As_2Se_3)_{95}I_5$) with standard deviation 2.5. Such a change in V_H corresponds to the change in nature and concentration of the chemical bonds favoured for each composition.

For the same quenching rate, the glass forming tendency differs for different materials. Hruby and Stourac [10] suggested an appropriate measure for the glass forming ability, that can be determined from DTA (DSC) of a glassy sample. This is defined as

$$K_{gl} = \left(T_{c_1} - T_g\right)\Big/\left(T_m - T_{c_1}\right),$$

where T_g is the glass transition temperatures, T_{c_1} and T_m are the start of the crystallization and melting temperatures respectively, in a DTA (DSC) thermogram. The values of K_{gl}'s of

As_2Se_3 and $(As_2Se_3)_{95}I_5$ which are obtained from their DSC scans at 20 deg/min, are 3.7 and 1.92 eV respectively.

The results indicate that $K_{gl} > 1$ for the two glasses and it decreases by adding I, which means that the tendency to form crystalline solids increases with the addition of iodine.

The activation energy of decomposition is useful for evaluating the thermal stability of materials. By plotting $\log \Phi$ *versus* $1/T$ and applying the least square fitting, E_d can be calculated (Figure 3). The E_d values obtained are 2 eV for As_2Se_3 and 1.08 eV for $(As_2Se_3)_{95}I_5$, which show that E_d decreases by adding I.

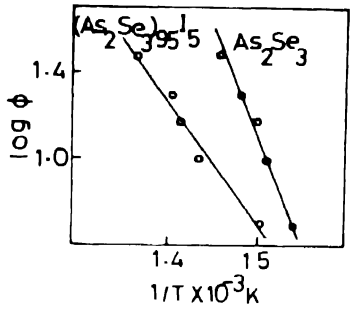

Figure 3. Plot of $\log\phi$ vs $1/T$

The decomposition energy is correlated with the type and strength of the possible chemical bonds. The chalcogenide glasses are predominantly covalent while the halide glasses are predominantly ionic in character. By adding iodine, the covalent nature of the bonds may get weakened which in turn, means that with the addition of iodine the glass needs less energy to decompose

The average heat of atomization $\overline{H}_s$ (in Kilocalorie per gram-atom) is defined for a compound $A_\alpha B_\beta C_\gamma$ as a direct measure of the cohesive energy and thus the average bond strength [11] can be given as

$$\overline{H}_s = \left(\alpha H_s^A + \beta H_s^B + \gamma H_s^C\right)/(\alpha+\beta+\gamma).$$

In the present work, $\overline{H}_s$ for As_2Se_3 and $(As_2Se_3)_{95}I_5$ are found to be equal to 57.54 and 57.016 K Cal/gm atom, respectively.

3.2. Electrical conduction :

The glasses As_2Se_3 and $(As_2Se_3)_{95}I_5$ have high resistivity at room temperature which makes measurements of conductivity very difficult at lower temperatures.

Figure 4 shows the plot of $\log\sigma$ *versus* $1/T$ for deposited film of As_2Se_3, which indicates a deviation from linearity at low temperatures $\approx$ 220 K. The value of the activation energy of conduction has been computed from the slope of least-square fits for the function

$\log\sigma = f(1/T)$. The value of ΔE and σ_0 estimated from the linear part in the temperature range 220–330 K, are 0.866 eV and $5.37 \times 10^2 (\Omega\,\text{cm})^{-1}$, respectively.

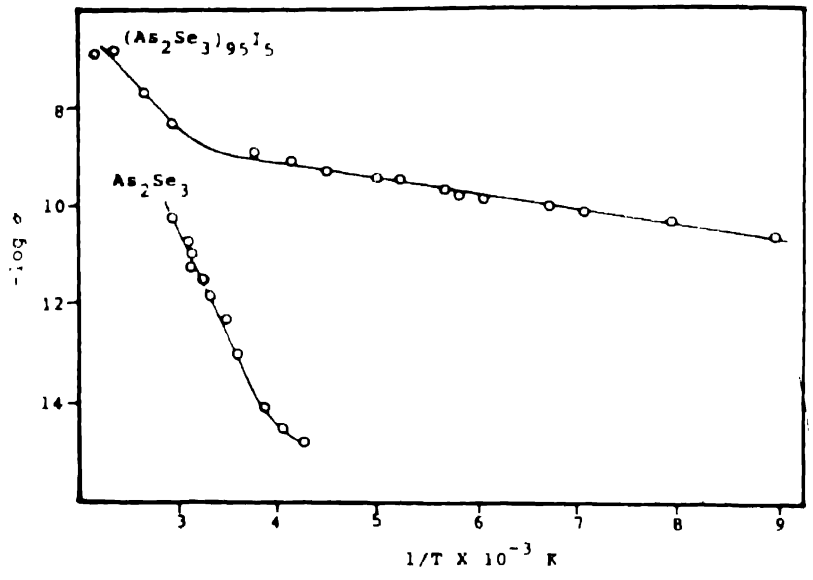

Figure 4. Temperature dependence of electrical conductivity of As_2Se_3 and $(As_2Se_3)_{95}I_5$ glasses.

For the deposited film of $(As_2Se_3)_{95}I_5$, the plot of the relation $\log\sigma = f(1/T)$ in the temperature range 160–333 K, exhibits two distinct slopes, showing two mechanisms of conduction. It was found that $\Delta E = 0.75$ eV and $\sigma_0 = 2.6 \times 10^2\ (\Omega\ \text{cm})^{-1}$ for the high temperature range (256–330 K) and $\Delta E = 0.24$ eV and $\sigma_1 = 2.016 \times 10^{-3}\ (\Omega\ \text{cm})^{-1}$ for the low temperature range (220–256 K).

The value of ΔE decreases in the order As_2Se_3 and $(As_2Se_3)_{95}I_5$. The gap of $(As_2Se_3)_{95}I_5$ seems to be closed by localized states band tails resulting from the compositional disorder created by the addition of I. This gives rise to the hopping conduction at lower temperatures as a second mechanism.

3.3. Optical absorption :

The absorption of light by amorphous solids depends on the energy ($h\nu$) of the incident photon and the optical gap E_g^{opt} of the material. For most amorphous semiconductors, this means photons in the visible region of the spectrum since their band gaps often lie in the range 1–3 eV. This behaviour can be explained by using the general equation adopted by Hasegawa *et al* [12], which relates the absorption coefficient (α) to the optical gap of amorphous solids.

$$(\hbar\nu\alpha)^n \propto (\hbar\nu - E_g^{opt}),$$

where α is the optical absorption coefficient.

Figure 5 shows the photon energy dependence of the absorption coefficient for the deposited film of $(As_2Se_3)_{95}I_5$ which indicates an exponential behaviour. It is clear that the optical absorption for amorphous semiconductors near absorption edge usually consists of

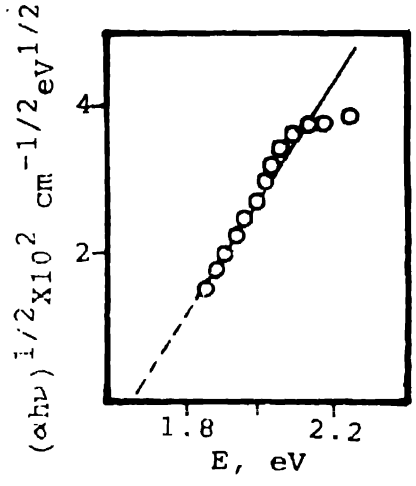

Figure 5. Dependence of $(\alpha h\nu)^{1/2}$ on photon energy for $(As_2Se_3)_{95}I_5$ glass

three regions [13]. Our results lie in the second region. This region corresponds to transitions between extended states in both valence and conduction bands and the absorption coefficient α is expressed as

$$\alpha = A(\hbar\nu - E_g^{opt})^2 / \hbar\nu,$$

where A is a constant.

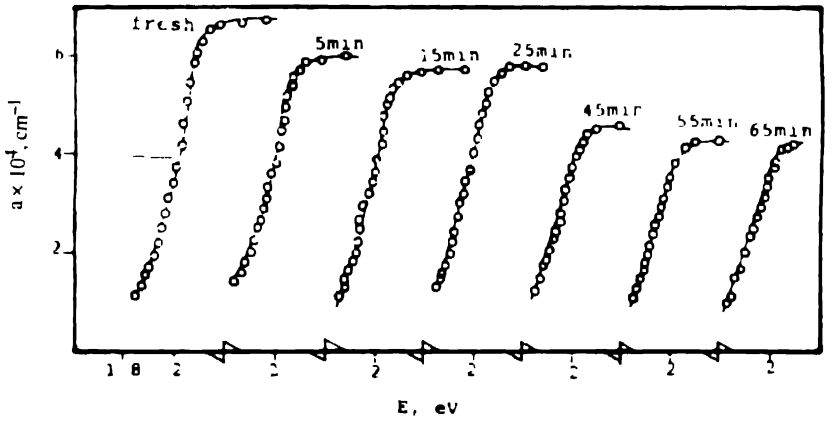

Figure 6. Absorption coefficient α of fresh and annealed $(As_2Se_3)_{95}I_5$

Thus, $(\alpha\hbar\nu)^{1/2}$ *vs* $\hbar\nu$ plot gives E_g^{opt} as the extrapolation value of $\hbar\nu$ intersecting $\alpha = 0$ which is equal to 1.66 eV. E_g^{opt} for As_2Se_3 is found to be 1.74 eV [11]. The addition of I to

As_2Se_3 creats more compositional disorder and consequently more localized state in the gap. The present of high density of localized states increases the transition probabilities and hence lowers the optical energy gap. So addition of I to As_2Se_3 decrease the width of the energy gap. This result is consistent with the results obtained from the conductivity experiments.

By annealing the sample at 160°C for different times (up to 65 min.), it is found that E_x^{opt} remains the same but the absorption coefficient decrease with time (Figure 6).

4. Conclusion

The chalcohalide glass $(As_2Se_3)_{95}I_5$ is found to have a high glass forming ability and interesting optical and electrical properties. Addition of small amounts of iodine to $(As_2Se_3)_{95}I_5$ is found to improve its optical and electrical properties and makes it more suitable for different applications.

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